

- 1 -

**INFLUENCE OF ACOUSTIC ENERGY ON COKE
MORPHOLOGY AND FOAMING IN DELAYED COKING**

FIELD OF THE INVENTION

[0001] This invention relates to a process for controlling coke morphology and foaming in delayed coking. More particularly, acoustic energy is used to control coke morphology and foaming in a delayed coking process.

BACKGROUND OF THE INVENTION

[0002] Delayed coking involves thermal decomposition of petroleum residua (resids) to produce gas, liquid streams of various boiling ranges, and coke. Delayed coking of resids from heavy and heavy sour (high sulfur) crude oils is carried out primarily as a means of disposing of these low value feedstocks by converting part of the resids to more valuable liquid and gaseous products. Although the resulting coke is generally thought of as a low value by-product, it may have some value, depending on its grade, as a fuel (fuel grade coke), electrodes for aluminum manufacture (anode grade coke), etc.

[0003] In the delayed coking process, the feedstock is rapidly heated in a fired heater or tubular furnace. The heated feedstock is then passed to a coking drum that is maintained at conditions under which coking occurs, generally at temperatures above 400°C under super-atmospheric pressures. One of the aspects of coke formation involves foam formation. In order to control foam formation, an anti-foam agent is typically added to the coke drum. Foam-overs in a coke drum are generally highly detrimental to the coking process.

- 2 -

[0004] The heated residuum feed in the coker drum also forms volatile components that are removed overhead and passed to a fractionator, leaving coke behind. When the coker drum is full of coke, the heated feed is switched to another drum and hydrocarbon vapors are purged from the coke drum with steam. The drum is then quenched with water to lower the temperature to less than 100°C after which the water is drained. When the cooling and draining steps are completed, the drum is opened and the coke is removed after drilling and/or cutting using high velocity water jets.

[0005] For example, a hole is typically bored through the center of the coke bed using water jet nozzles located on a boring tool. Nozzles oriented horizontally on the head of a cutting tool then cut the coke from the drum. The coke removal step adds considerably to the throughput time of the overall process. Thus, it would be desirable to be able to produce a free-flowing coke, in a coker drum, that would not require the expense and time associated with conventional coke removal.

[0006] Even though the coker drum may appear to be completely cooled, areas of the drum do not completely cool. This phenomenon, sometimes referred to as "hot drum", may be the result of a combination of morphologies of coke being present in the drum, which may contain a combination of more than one type of solid coke product, i.e., needle coke, sponge coke and shot coke. Since unagglomerated shot coke may cool faster than other coke morphologies, such as large shot coke masses or sponge coke, it would be desirable to produce predominantly substantially free-flowing shot coke in a delayed coker, in order to avoid or minimize hot drums.

[0007] Coke morphology is difficult to proactively control as coke formation is not an exact science. For example, crude selection may influence coke

- 3 -

morphology. However, it is difficult to predict in advance exactly what influence the make-up of any give crude will have on the morphology of coke produced. Other process variables may be adjusted, but it is still very difficult to control the coking process to make a certain type of coke while excluding other types of coke. There is a need to be able to proactively control coke morphology.

SUMMARY OF THE INVENTION

[0008] One embodiment of the invention relates to a method for controlling coke morphology in a delayed coking process that comprises: (a) heating a coker feedstock in a heater to produce a heated feedstock, (b) conducting the heated feedstock to a coker vessel, (c) maintaining the coker vessel at delayed coking temperatures at effective delayed coking conditions to produce vapor products and coke, (d) quenching the coker vessel, and (e) subjecting at least one of steps (a), (b) or (c) to acoustic energy at an energy level and for a time sufficient to produce shot coke.

[0009] Another embodiment relates to a method for controlling foam formation in a delayed coking process that comprises: (a) heating a coker feedstock in a heater to produce a heated feedstock, (b) conducting the heated feedstock to a coker vessel, (c) maintaining the coker vessel at delayed coking temperatures at effective delayed coking conditions to produce foam, vapor products and coke, and (d) subjecting the coker vessel in step (c) to acoustic energy at an energy level and for a time sufficient to reduce the amount of foam.

- 4 -

DETAILED DESCRIPTION OF THE INVENTION

[0010] Petroleum atmospheric or vacuum residua ("resid") feedstocks are suitable for delayed coking. Such petroleum residua are frequently obtained after removal of distillates from crude feedstocks and are characterized as being comprised of components of large molecular size and weight, generally containing: (a) asphaltenes and other high molecular weight aromatic structures that would inhibit the rate of hydrotreating/hydrocracking and cause catalyst deactivation; (b) metal contaminants occurring naturally in the crude or resulting from prior treatment of the crude, which contaminants would tend to deactivate hydrotreating/hydrocracking catalysts and interfere with catalyst regeneration; and (c) a relatively high content of sulfur and nitrogen compounds that give rise to objectionable quantities of SO₂, SO₃, and NO_x upon combustion of the petroleum residuum. Nitrogen compounds present in the resid also have a tendency to deactivate catalytic cracking catalysts.

[0011] Resid feedstocks include, but are not limited to, residues from the atmospheric and vacuum distillation of petroleum crudes or the atmospheric or vacuum distillation of heavy oils, visbroken resids, tars from deasphalting units or combinations of these materials. Atmospheric and vacuum-topped heavy bitumens can also be employed. Typically, such feedstocks are high-boiling hydrocarbonaceous materials having a nominal initial boiling point of 538°C or higher, an API gravity of 20° or less, and a Conradson Carbon Residue content of 0 to 40 weight percent.

[0012] The resid feed is subjected to delayed coking. Generally, in delayed coking, a residue fraction, such as a petroleum residuum feedstock, is pumped to a heater at a pressure of 50 to 550 psig (446 to 3893 kPa), where it is heated to a

- 5 -

temperature from 480°C to 520°C. The heater comprises one or more furnaces containing one or more furnace tubes.

[0013] The heated feedstock from the furnace is then conducted into a coking zone containing one or more vessels through at least one transfer line. The transfer line may be heated if necessary. The coking vessel is typically a vertically-oriented, insulated coker drum and heated feedstock is transferred into the coker drum through an inlet at or near the base of the drum. Coker drums may be run in tandem so that while one drum is in operation, the other may be in the process of having coke removed. Pressure in the drum is usually relatively low, such as 15 to 80 psig to allow volatiles to be removed overhead. Typical operating temperatures of the drum will be between 410°C and 475°C. The hot feedstock thermally cracks over a period of time (the "coking time") in the coker drum, liberating volatiles composed primarily of hydrocarbon products that continuously rise through the coke mass and are collected overhead. The volatile products are sent to a coker fractionator for distillation and recovery of coker gases, gasoline, light gas oil, and heavy gas oil. In an embodiment, a portion of the heavy coker gas oil present in the product stream introduced into the coker fractionator can be captured for recycle and combined with the fresh feed (coker feed component), thereby forming the coker heater or coker furnace charge. In addition to the volatile products, delayed coking also forms solid coke product.

[0014] There are generally three different types of solid delayed coker products that have different values, appearances and properties, i.e., needle coke, sponge coke, and shot coke. Needle coke is the highest quality of the three varieties. Needle coke, upon further thermal treatment, has high electrical conductivity (and a low coefficient of thermal expansion) and is used in electric arc steel production. It is relatively low in sulfur and metals and is frequently produced from some of the

- 6 -

higher quality coker feedstocks that include more aromatic feedstocks such as slurry and decant oils from catalytic crackers and thermal cracking tars. Typically, it is not formed by delayed coking of resid feeds.

[0015] Sponge coke, a lower quality coke, is most often formed in refineries. Lower quality refinery coker feedstocks having significant amounts of asphaltenes, heteroatoms and metals produce this lower quality coke. If the sulfur and metals content is low enough, sponge coke can be used for the manufacture of electrodes for the aluminum industry. If the sulfur and metals content is too high, then the coke can be used as fuel. The name "sponge coke" comes from its porous, sponge-like appearance. Conventional delayed coking processes, using the preferred vacuum resid feedstock of the present invention, will typically produce sponge coke, which is produced as an agglomerated mass that needs an extensive removal process including drilling and water-jet technology. As discussed, this considerably complicates the process by increasing the cycle time.

[0016] Shot coke is considered the lowest quality coke. The term "shot coke" comes from its shape which is similar to that of BB-sized balls. Desirable shots may be in the range of 1 to 10 mm in diameter. Shot coke, like the other types of coke, has a tendency to agglomerate, especially in admixture with sponge coke, into larger masses, sometimes larger than a foot in diameter. This can cause refinery equipment and processing problems. Shot coke is usually made from the lowest quality high resin-asphaltene feeds and makes a good high sulfur fuel source, particularly for use in cement kilns and steel manufacture. There is also another coke, which is referred to as "transition coke" and refers to a coke having a morphology between that of sponge coke and shot coke. For example, coke that has a mostly sponge-like physical appearance, but with evidence of small shot

- 7 -

spheres beginning to form as discrete shapes. The term "transition coke" can also refer to mixtures of shot coke bonded together with sponge coke.

[0017] Foam is usually formed in the delayed coking process. Foam-over results when the delayed coker drum contains excessive foam and can result in numerous problems such as partial plugging of lines, coke lay-down, plugged heater tubes and the like. Foam-over is typically controlled by operational constraints on the coking process itself, by the addition of antifoam additives such as silicone based chemicals, or both. Thus coke drums are not utilized to their full capacity in order to leave room for foam formation. In addition to or in the alternative, siloxanes are injected into the over head of the coke drum to control excess foam formation. Anti-foam agents may also be non-silicone based, including, for example, organic sulfonates, phenates, salicylates, carbon powders, oils (animal and vegetable) and polymers such as polyolefins, e.g., polyisobutylenes.

[0018] The present invention addresses both control of coke morphology and foam formation by using acoustic energy during the coking process. Acoustic generators generate acoustic energy in the form of sound waves to control both coke morphology and foam formation. To control coke morphology, the sound waves may be oriented in the direction axially along the length of the coker drum, across the diameter of the drum, i.e., perpendicular to the axis of the drum or some angle in between. The acoustic energy may be applied to at least one of the drum itself, to furnace tubes, or transfer lines. To control foam formation, sound waves are preferably applied across the diameter of the coke drum. The sound waves may be applied in conjunction with chemical anti-foam additives to control foam formation.

- 8 -

[0019] For the present control of coke morphology and foam formation, the sound (acoustic) waves are in the frequency range from 15 to 20,000 Hertz (Hz), preferably from 50 to 10,000 Hz. The sound intensity, which is a measure of the acoustic energy transmitted to the aerosol mist, is in the range from 90 to 200 decibels (dB), preferably 120 to 150 dB. The duration of the sound waves is for a time sufficient to cause the desired degree of control of coke morphology and foam formation. This is typically in the range of 1 to 10 seconds and depends on the operating conditions within the coker unit. It is preferred to adapt the sound wave frequency, acoustic energy and the geometry of the coker system to achieve a standing wave condition. The sound generators may be oriented perpendicular to the coker drum or may be oriented at an angle varying from perpendicular to parallel with the axis of the coker drum. The type of acoustic generator may be any of a variety of commercially available sound generators such as transducers, sirens, air horns, electromagnetic sonic devices and the like. The duration of application of acoustic energy is preferably from the inception of filling of the coke drum to completion of the filling of the coke drum to the desired level. However, the application of acoustic energy may be either intermittent or for some period less than the full filling cycle.

[0020] In an embodiment, shot coke formation may be enhanced by treating the residuum feedstock with one or more metal-containing additives in addition to the application of acoustic energy. The additives are those that enhance the production of shot coke during delayed coking. A resid feed is subjected to treatment with one or more additives, at effective temperatures, i.e., at temperatures that will encourage the additives' dispersal in the feed stock. Such temperatures will typically be from 70°C to 500°C, preferably from 150°C to 370°C, more preferably from 185°C to 350°C. The additive suitable for use herein can be liquid or solid form, with liquid/solution form being preferred. Non-limiting examples of metals-

- 9 -

containing additives include metal hydroxides, naphthenates and/or carboxylates, metal acetylacetonates, Lewis acids, a metal sulfide, metal acetate, metal carbonate, high surface area metal-containing solids, inorganic oxides and salts of oxides; salts that are basic are preferred. Non-limiting examples of substantially metals-free additives that can be used in the practice of the present invention include elemental sulfur, high surface area substantially metals-free solids, such as rice hulls, sugars, cellulose, ground coals, ground auto tires; inorganic oxides such as fumed silica and alumina; salts of oxides, such as ammonium silicate and mineral acids such as sulfuric acid, phosphoric acid, and acid anhydrides. These additives are disclosed in WO 2004104139, which is incorporated herein by reference.

[0021] While not wishing to be bound to any particular theory, one explanation for shot coke formation is that shots are formed in the coker furnace and transfer line when the heaviest and most polar components (highest solubility parameter components) of the resid feedstock begin to come out of a primary lower solubility parameter liquid phase and start to form a second liquid phase. Depending on nucleation sites, coalescence sites, and process shear and turbulence conditions, the second liquid phase can coalesce and grow into spherical particles of a heavy tar the subsequently dry into hard spheres. In the present invention, the application of acoustic energy facilitates the coalescence of the second liquid phase components into uniform spheres, preferably having a diameter of from 0.5 to 5 mm. In addition, the application of acoustic energy helps collapse the foam and, if used in conjunction with anti-foam agents, increases the effectiveness of the anti-foam agents.

- 10 -

[0022] The invention is further illustrated in the following non-limiting examples.

EXAMPLES

[0023] The following examples are based on modeling studies.

Example 1

[0024] A heavy Canadian vacuum resid blend produces a mixture of shot (15%) and shot coke bonded to sponge coke in the drum of a commercial delayed coker. Use of transducer devices to introduce standing sound waves into the last four tubes of the furnace and through the transfer line increases the amount of shot coke to 80%. Introducing standing waves into the furnace tubes, transfer line and coke drum increases shot coke to 95%.

Example 2

[0025] Use if the feed of Example 1 produces a foam height of 15 feet (4.6 m) in the drum midway through the fill cycle. Introduction of silicone antifoam knocks the foam height back to 5 to 10 feet (1.5 to 3 m). Application of standing sound wave to the drum helps to collapse the foam and also increases antifoam effectiveness such that only 1/3 the amount of antifoam gives the same 5 to 10 feet (1.5 to 3 m) foam height.

- 11 -

CLAIMS:

1. A method for controlling coke morphology in a delayed coking process that comprises:
 - (a) heating a coker feedstock in a heater to produce a heated feedstock,
 - (b) conducting the heated feedstock to a coker vessel,
 - (c) maintaining the coker vessel at delayed coking temperatures at effective delayed coking conditions to produce vapor products and coke,
 - (d) quenching the coker vessel, and
 - (e) subjecting at least one of steps (a), (b), or (c) to acoustic energy at an energy level and for a time sufficient to produce shot coke.
2. A method for controlling foam formation in a delayed coking process that comprises:
 - (a) heating a coker feedstock in a heater to produce a heated feedstock,
 - (b) conducting the heated feedstock to a coker vessel,
 - (c) maintaining the coker vessel at delayed coking temperatures at effective delayed coking conditions to produce foam, vapor products and coke, and
 - (d) subjecting the coker vessel in step (c) to acoustic energy at an energy level and for a time sufficient to reduce the amount of foam.
3. The method of any preceding claim wherein the feedstock is heated to temperatures of 480°C to 520°C in at least one furnace containing at least one furnace tube and is transferred to the coker vessel through at least one transfer line.

- 12 -

4. The method of claims any preceding claim wherein the coke formed is a sponge coke, shot coke or mixture thereof.

5. The method of any preceding claim further comprising at least one metal-containing additive.

6. The method of claim 2 wherein at least one anti-foam agent is added to the coker vessel.

7. The method of any preceding claim wherein acoustic energy is applied to at least one of the coker drum, furnace tube or transfer line.

8. The method of any preceding claim wherein the acoustic energy is applied axially along the length of the coker vessel, across the diameter of the coker vessel or at some angle between axial and perpendicular to axial.

9. The method of any preceding claim wherein the acoustic energy is in a frequency range from 15 to 20,000 Hz.

10. The method of any preceding claim wherein the acoustic energy is in the range from 90 to 200 dB and is in the form of a standing wave.